# Synthesis, $^{9}$Be NMR Spectroscopy, and Structural Characterization of Sterically Encumbered Beryllium Compounds

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*Received March 18, 1997*⊗

The use of the terphenyl substituent $-C_6H_3$-2,6-$Mes_2$ (abbreviated Ar) has permitted the synthesis of several new low-coordinate beryllium compounds. Reaction of 1 equiv of LiAr with $BeCl_2(OEt_2)_2$ or $BeBr_2(OEt_2)_2$ (**1**) gives the monomeric complexes $ArBeX(OEt_2)$ (X = Cl (**2**); Br (**3**) featuring three-coordinate berylliums. Treatment of **2** with 1 equiv of LiSMes* (Mes* = $-C_6H_2$-2,4,6-*t*-$Bu_3$) affords the three-coordinate thiolate derivative ArBeSMes*$(OEt_2)$ (**4**). The reaction of **2** with LiNHPh, $LiNHSiPh_3$, or $LiN(SiMe_3)_2$ affords the unstable dimer $(ArBeNHPh)_2$ (**5**) or the monomers $ArBeNHSiPh_3(OEt_2)$ (**6**) and $ArBeN(SiMe_3)_2$ (**7**). The last is the first example of a two-coordinate beryllium center in the solid state. The addition of 1 equiv of **2** to $NaMo(\eta^5\text{-}C_5H_5)(CO)_3$ gives the isocarbonyl complex $Ar(THF)_2Be(OC)_3Mo(\eta^5\text{-}C_5H_5)$ (**8**), which features four-coordinate beryllium bound to Ar, two THF ligands, and an oxygen from one of the molybdenum-bound carbonyls. Reaction of **2** with a 1:1 mixture of $LiN(SiMe_3)_2$ and PhCN affords the six-membered-ring compound $PhC(NSiMe_3)_2(BeCl)_2N(SiMe_3)_2$ (**9**) and the four-coordinate monomer $Be\{(NSiMe_3)_2CPh\}_2$ (**10**). Compounds **1**−**10** were characterized by X-ray crystallography, and **1** and **4** and **6**−**10** were also characterized by $^{1}$H, $^{9}$Be, and $^{13}$C NMR spectroscopy. X-ray data at 130 K (**1**−**9**) or 185 K (**10**) with Mo Kα ($\lambda$ = 0.710 73 Å) (**1**, **2a**, **3**, **7**, **8**) or Cu Kα ($\lambda$ = 1.541 78 Å) (**2b**, **4**−**6**, **9**, **10**). $BeBr_2(OEt_2)_2$ (**1**), $a$ = 11.690(5) Å, $b$ = 10.191(3) Å, $c$ = 12.131(5) Å, $\beta$ = 114.67(3)°, $V$ = 1313.3(9) Å$^3$, space group $P2_1/n$, $Z$ = 4, $R_1$ = 0.062; $ArBeCl(OEt_2)$ (**2a**), $a$ = 13.136(3) Å, $b$ = 13.877(3) Å, $c$ = 28.092(6) Å, $V$ = 5121(2) Å$^3$, space group *Pbca*, $Z$ = 8, $R_1$ = 0.058; $ArBeCl(OEt_2)$ (**2b**), $a$ = 8.857(1) Å, $b$ = 8.8977(9) Å, $c$ = 18.198(7) Å, α = 86.437(8)°, $\beta$ = 82.677(8)°, $\gamma$ = 62.405(7)°, $V$ = 1260.5(2) Å$^3$, space group $P\bar{1}$, $Z$ = 2, $R_1$ = 0.048; $ArBeBr(OEt_2)$ (**3**), $a$ = 8.873(5) Å, $b$ = 8.847(5) Å, $c$ = 18.251(7) Å, α = 86.54(4)°, $\beta$ = 83.17(4)°, $\gamma$ = 64.14(4)°, $V$ = 1280(1) Å$^3$, space group $P\bar{1}$, $Z$ = 2, $R_1$ = 0.071; ArBeSMes*-$(OEt_2)\cdot 0.5C_6H_{14}$ (**4**$\cdot 0.5C_6H_{14}$), $a$ = 9.732(1) Å, $b$ = 11.190(1) Å, $c$ = 21.841(2) Å, α = 75.225(7)°, $\beta$ = 81.137(8)°, $\gamma$ = 73.382(8)°, $V$ = 2195.3(4) Å$^3$, space group $P\bar{1}$, $Z$ = 2, $R_1$ = 0.062; $(ArBeNHPh)_2\cdot C_4H_{10}O$ (**5**$\cdot C_4H_{10}O$), $a$ = 11.894(2) Å, $b$ = 12.212(2) Å, $c$ = 18.709(3) Å, $\beta$ = 99.24(1)°, $V$ = 2682.4(7) Å$^3$, space group $P2_1$, $Z$ = 2, $R_1$ = 0.045; $ArBeNHSiPh_3(OEt_2)$ (**6**), $a$ = 11.959(2) Å, $b$ = 16.655(2) Å, $c$ = 19.718(2) Å, $\beta$ = 105.368(9)°, $V$ = 3786.9(8) Å$^3$, space group $P2_1/c$, $Z$ = 4, $R_1$ = 0.047; $ArBeN(SiMe_3)_2$ (**7**), $a$ = 12.623(3) Å, $b$ = 15.404(4) Å, $c$ = 15.502(3) Å, $V$ = 3014(1) Å$^3$, space group *Pbcn*, $Z$ = 4, $R_1$ = 0.046; $Ar(THF)_2Be(OC)_3Mo$-$(\eta^5\text{-}C_5H_5)\cdot 2C_7H_8$ (**8**$\cdot 2C_7H_8$), $a$ = 19.111(4) Å, $b$ = 11.976(3) Å, $b$ = 21.241(5) Å, $\beta$ = 103.47(2)°, $V$ = 4728(2) Å$^3$, space group $P2_1/c$, $Z$ = 4, $R_1$ = 0.049; $PhC(NSiMe_3)_2(BeCl)_2N(SiMe_3)_2$ (**9**), $a$ = 19.996(4) Å, $b$ = 14.816(2) Å, $c$ = 20.183(4) Å, $V$ = 5979(2)Å$^3$, space group *Pbca*, $Z$ = 8, $R_1$ = 0.043; $Be\{(NSiMe_3)_2CPh\}_2$ (**10**), $a$ = 20.022(2) Å, $b$ = 9.7161(9) Å, $c$ = 19.456(2) Å, $\beta$ = 11.392(8)°, $V$ = 3524.1(6) Å$^3$, space group $P2_1/c$, $Z$ = 4, $R_1$ = 0.075.

## Introduction

The chemistry of beryllium is relatively unexplored compared to that of its neighboring elements.[1] This is due to its high toxicity,[2] which acts as a deterrent to the experimentalist if not the theoretician. Its position as a first-row element and its relatively small size suggest a rich chemistry involving, inter alia, compounds with more covalent character than their heavier congeners or compounds that involve multiple bonding to beryllium. Although a significant degree of covalent character in many beryllium compounds is well-established,[1,3] multiple bonding has not been substantiated to any great degree. In this paper, the synthesis of several sterically encumbered arylberyllium derivatives of the terphenyl ligand $-C_6H_3$-2,6-$Mes_2$ (Mes = $-C_6H_2$-2,4,6-$Me_3$) is reported. The presence of large substituents is often a requirement for the stabilization of multiple interactions in main group compounds involving elements other than carbon, nitrogen, oxygen or sulfur. Even though the new compounds **1**−**10** have not yet led to the isolation of any multiply-bonded or catenated species involving beryllium, it is shown that the $-C_6H_3$-2,6-$Mes_2$ (abbreviated Ar) substituent induces considerable crowding at the beryllium centers and has enabled previously uncharacterized types of compounds to be isolated.

## Experimental Section

**Preparation of Compounds.** All reactions were performed by using modified Schlenk techniques under an inert atmosphere of $N_2$ or a Vacuum Atmospheres HE43-2 drybox. Solvents were freshly distilled under $N_2$ from a Na/K alloy and degassed twice before use. The compounds $(LiC_6H_3\text{-}2,6\text{-}Mes_2)_2$,[4] i.e. $(LiAr)_2$, $H_2NSiPh_3$,[5] HSMes*[6] (Mes* = 2,4,6-*t*-$Bu_3C_6H_2$−), and $LiN(SiMe_3)_2$[7] were synthesized by literature procedures. Beryllium metal and $BeCl_2$ were purchased from

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⊗ Abstract published in *Advance ACS Abstracts,* September 1, 1997.

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S0020-1669(97)00319-4 CCC: $14.00

commercial suppliers and used as received. *Caution*: Beryllium and beryllium compounds are extremely toxic and should be handled with great care. NMR spectra were recorded in $C_6D_6$ solution by using a General Electric QE-300 spectrometer and, in the case of $^9$Be NMR, were referenced to external $Be(NO_3)_2$ in aqueous solution; IR spectra (Nujol mull, CsI plates) were obtained in the range 4000−200 $cm^{-1}$ with a Perkin-Elmer 1420 spectrometer.

**$BeBr_2(OEt_2)_2$ (1).** Diethyl ether (*ca.* 60 mL) was added to a mixture of beryllium metal powder (0.09 g, 10.0 mmol) and $HgBr_2$ (2.16 g, 6.0 mmol), and the reaction mixture was allowed to stir overnight. The supernatant solution was separated from the mercury and beryllium metals via a cannula. The volume was reduced to incipient crystallization, and the solution was cooled in a −20 °C freezer to give **1** as colorless crystals. Crystals suitable for X-ray crystallographic studies were obtained by cooling slowly a saturated solution of **1** in diethyl ether to 5 °C. Yield: 1.56 g (82%). $^1$H NMR ($C_6D_6$): $\delta$ 1.04 (t, $\mathrm{OCH_2C}H_3$), 3.90 (q, $\mathrm{OC}H_2\mathrm{CH_3}$). $^{13}$C NMR ($C_6D_6$): $\delta$ 13.5 ($\mathrm{OCH_2}C\mathrm{H_3}$), 68.0 ($\mathrm{O}C\mathrm{H_2CH_3}$). $^9$Be NMR ($C_6D_6$): $\delta$ 3.0.

**ArBeCl($OEt_2$) (2).** With stirring, a solution of LiAr (5.49 g, 17.2 mmol) in *ca.* 70 mL of diethyl ether was added dropwise to a suspension of $BeCl_2$ (1.37 g, 17.1 mmol) in *ca.* 20 mL of diethyl ether. Stirring was continued at ambient temperature overnight, and the solvent was removed under reduced pressure. The remaining colorless solid was extracted with *ca.* 30 mL of toluene, and the mixture was filtered over a Celite-padded frit. The volume of the filtrate was reduced to incipient crystallization, and the solution was cooled in a −20 °C freezer to give **2a** as large colorless crystals. Crystals of the polymorphic compound **2b** were obtained by crystallization from diethyl ether. Yield: 62−71%. Mp: 145−147 °C. $^1$H NMR ($C_6D_6$): $\delta$ 0.35 (t, $\mathrm{OCH_2C}H_3$), 2.20 ($p$-$\mathrm{C}H_3$), 2.28 ($o$-$\mathrm{C}H_3$), 3.37 (q, $\mathrm{OC}H_2\mathrm{CH_3}$), 6.87 (*m*-Mes), 7.05 (d, $m$-$C_6H_3$), 7.34 (t, $p$-$C_6H_3$). $^{13}$C NMR ($C_6D_6$): $\delta$ 12.9 ($\mathrm{OCH_2}C\mathrm{H_3}$), 21.1 ($p$-$C\mathrm{H_3}$), 21.6 ($o$-$C\mathrm{H_3}$), 68.4 ($\mathrm{O}C\mathrm{H_2CH_3}$), 126.1 ($m$-$C_6H_3$), 127.4 ($p$-$C_6H_3$), 128.5 (*m*-Mes), 135.7 (*p*-Mes), 136.5 (*o*-Mes), 143.5 (*i*-Mes), 149.5 ($o$-$C_6H_3$), 153.2 ($i$-$C_6H_3$). $^9$Be NMR ($C_6D_6$, 20 °C [70 °C]): $\delta$ 12.8 [12.5] ($w_{1/2}$ = 315 [150] Hz). IR (Nujol, $cm^{-1}$): 1723 w, 1602 m, 1563 w, 1539 m, 1319 w, 1280 w, 1221 w, 1187 m, 1151 w, 1142 ms, 1116 s, 1085 m, 1072 m, 1049 m, 1002 vs, 985 sh, 885 s, 849 vs, 809 sh, 801 s, 776 s, 703 vs, 652 m, 562 w, 540 w, 475 m, 374 m, 326 w.

**ArBeBr($OEt_2$) (3).** The synthesis was accomplished in a manner similar to the preparation of **2** with use of LiAr (1.16 g, 3.63 mmol) and $BeBr_2(OEt_2)_2$ (1.15 g, 3.63 mmol). Crystals suitable for X-ray crystallographic studies were grown from diethyl ether. Yield: 1.11 g (64%). Mp: 160−162 °C. $^1$H NMR ($C_6D_6$): $\delta$ 0.35 (t, $\mathrm{OCH_2C}H_3$), 2.20 ($p$-$\mathrm{C}H_3$), 2.30 ($o$-$\mathrm{C}H_3$), 3.40 (q, $\mathrm{OC}H_2\mathrm{CH_3}$), 6.88 (*m*-Mes), 7.04 (d, $m$-$C_6H_3$), 7.35 (t, $p$-$C_6H_3$). $^{13}$C NMR ($C_6D_6$): $\delta$ 13.1 ($\mathrm{OCH_2}C\mathrm{H_3}$), 21.2 ($p$-$C\mathrm{H_3}$), 21.8 ($o$-$C\mathrm{H_3}$), 69.2 ($\mathrm{O}C\mathrm{H_2CH_3}$), 126.2 ($m$-$C_6H_3$), 127.5 ($p$-$C_6H_3$), 128.5 (*m*-Mes), 135.8 (*p*-Mes), 136.5 (*o*-Mes), 143.2 (*i*-Mes), 149.5 ($o$-$C_6H_3$), 153.1 ($i$-$C_6H_3$). $^9$Be NMR ($C_6D_6$, 20 °C [70 °C]): $\delta$ 13.4 [13.0] ($w_{1/2}$ = 245 [145] Hz). IR (Nujol, $cm^{-1}$): 1608 m, 1561 w, 1541 m, 1283 w, 1228 w, 1191 m, 1166 sh, 1150 m, 1121 ms, 1092 m, 1177 sh, 1053 sh, 1012 vs, 992 sh, 893 s, 849 vs, 805 s, 777 s, 737 m, 715 w, 680 s, 653 m, 617 m, 599 sh, 572 m, 483 m, 369 m.

**ArBeSMes*($OEt_2$)·0.5$C_6H_{14}$ (4·0.5$C_6H_{14}$).** A solution of LiSMes* in *ca.* 15 mL of diethyl ether, freshly prepared from HSMes* (0.39 g, 1.39 mmol) and *n*-BuLi (0.87 mL of a 1.6 M solution in *n*-hexane), was added to a solution of **2** (0.60 g, 1.39 mmol) in *ca.* 15 mL toluene. Stirring was continued at ambient temperature for 4 h, after which the solvent was removed under reduced pressure. The remaining solid was extracted with *ca.* 20 mL of *n*-hexane, and the extract was filtered. Reduction of the volume to *ca.* 5 mL and cooling to *ca.* 5 °C afforded colorless crystals of compound **4**. Yield: 0.57 g (57%). Mp: 184−185 °C (desolvation at *ca.* 60 °C). $^1$H NMR ($C_6D_6$): $\delta$ 0.35 (t, $\mathrm{OCH_2C}H_3$), 0.88 (m, $C_6H_{14}$), 1.25 ($p$-$\mathrm{C(C}H_3)_3$), 1.52 ($o$-$\mathrm{C(C}H_3)_3$), 2.29 ($p$-$\mathrm{C}H_3$), 2.30 ($o$-$\mathrm{C}H_3$), 3.15 (q, $\mathrm{OC}H_2\mathrm{CH_3}$), 6.90 (*m*-Mes), 6.96 (d, $m$-$C_6H_3$), 7.30 (t, $p$-$C_6H_3$), 7.37 (*m*-Mes*). $^{13}$C NMR ($C_6D_6$): $\delta$ 12.5 ($\mathrm{OCH_2}C\mathrm{H_3}$), 14.3, 23.0, 32.0 ($C_6\mathrm{H_{14}}$), 21.2 ($p$-$C\mathrm{H_3}$), 22.0 ($o$-$C\mathrm{H_3}$), 31.6 ($p$-$\mathrm{C(}C\mathrm{H_3)_3}$), 32.2 ($o$-$\mathrm{C(}C\mathrm{H_3)_3}$), 34.6 ($p$-$C\mathrm{(CH_3)_3}$), 38.1 ($o$-$C\mathrm{(CH_3)_3}$), 67.6 ($\mathrm{O}C\mathrm{H_2CH_3}$), 121.5 (*m*-Mes*), 127.0 ($m$-$C_6H_3$), 127.3 ($p$-$C_6H_3$), 129.0 (*m*-Mes), 135.2 (*p*-Mes), 135.6 (*i*-Mes*), 136.2 (*o*-Mes), 144.1 (*i*-Mes), 145.6 (*p*-Mes*), 150.3 ($o$-$C_6H_3$), 153.0 (*o*-Mes*). $^9$Be NMR ($C_6D_6$, 20 °C [70 °C]): $\delta$ 17.4 [17.1] ($w_{1/2}$ = 540 [260] Hz). IR (Nujol, $cm^{-1}$): 1608 m, 1592 m, 1564 w, 1543 m, 1360 sh, 1350 sh, 1315 w, 1283 w, 1258 w, 1240 m, 1212 m, 1190 w, 1183 sh, 1167 sh, 1149 m, 1114 ms, 1088 m, 1072 w, 1047 m, 1024 vs, 990 m, 922 vw, 886 s, 875 sh, 848 vs, 807 ms, 779 vs, 759 m, 742 m, 719 vs, 649 m, 566 w, 549 sh, 478 w, 442 vw, 384 w, 330 vw.

**$(ArBeNHPh)_2$·$OEt_2$ (5·$OEt_2$).** With stirring, *n*-BuLi (0.83 mL of a 1.6 M solution in *n*-hexane) was added at *ca.* 0 °C to a solution of aniline (0.12 mL, 1.32 mmol) in *ca.* 25 mL of diethyl ether, and the solution was warmed to ambient temperature. After 2 h, **2** (0.39 g, 1.39 mmol) was added via a solids-addition tube, and stirring was continued for another 2 h. The mixture was then filtered, and the volume of the filtrate was reduced to incipient crystallization. Cooling in a −20 °C freezer afforded a 60:40 mixture of large colorless crystals (**5**·$OEt_2$) and smaller colorless crystals which proved to be ArH. Some of the crystals were removed from the mother liquor and were used for X-ray crystallographic studies. The mother liquor was then removed via a cannula and the remaining crystals were dried under reduced pressure to give a white, noncrystalline solid. An IR spectrum of the solid showed no N−H vibrations. A solution in $C_6D_6$ was characterized by $^1$H and $^{13}$C NMR spectroscopy, showing only the characteristic data for Ar H. Apparently, 50% of the solid ($\{BeNPh\}_x$) remained insoluble in $C_6D_6$.

**$ArBeNHSiPh_3(OEt_2)$ (6).** A solution of $LiNHSiPh_3$ in *ca.* 20 mL of diethyl ether, freshly prepared from $H_2NSiPh_3$ (0.36 g, 1.30 mmol) and *n*-BuLi (0.82 mL of a 1.6 M solution in *n*-hexane), was added with stirring to a solution of **2** (0.56 g, 1.30 mmol) in *ca.* 15 mL of diethyl ether. Stirring was continued at ambient temperature overnight, whereupon the mixture was filtered over a Celite-padded filter frit. The volume of the filtrate was reduced to *ca.* 20 mL, and cooling in a −20 °C freezer afforded the product **6** as colorless crystals suitable for X-ray crystallography. Yield: 0.59 g (68%). Mp: softens >146 °C, melts 155−170 °C. $^1$H NMR ($C_6D_6$): $\delta$ 0.12 (t, $\mathrm{OCH_2C}H_3$), 2.17 ($o$-$\mathrm{C}H_3$), 2.33 ($p$-$\mathrm{C}H_3$), 3.09 (q, $\mathrm{OC}H_2\mathrm{CH_3}$), 6.90 (*m*-Mes), 7.06 (d, $m$- $C_6H_3$), 7.20 (d, $o$-$SiC_6H_5$), 7.34 (t, $p$-$C_6H_3$), 7.57 (m, $m$-$SiC_6H_5$). $^{13}$C NMR ($C_6D_6$): $\delta$ 12.1 ($\mathrm{OCH_2}C\mathrm{H_3}$), 21.3 ($p$-$C\mathrm{H_3}$), 21.6 ($o$-$C\mathrm{H_3}$), 66.3 ($\mathrm{O}C\mathrm{H_2CH_3}$), 126.0 ($m$-$C_6H_3$), 126.6 ($p$-$C_6H_3$), 128.5 (*m*-Mes), 135.3 (*p*-Mes), 136.2 (*o*-Mes), 144.7 (*i*-Mes), 149.7 ($o$-$C_6H_3$), 156.8 ($i$-$C_6H_3$), 127.7, 128.8, 135.8, 140.5 ($SiPh_3$). $^9$Be NMR ($C_6D_6$, 70 °C): $\delta$ 12.6 ($w_{1/2}$ = 285 Hz). IR (Nujol, $cm^{-1}$): 1609 w, 1595 vw, 1300 vw, 1259 m, 1228 vw, 1112 s, 1085 sh, 1020 ms, 848 m, 799 s, 735 m, 712 sh, 699 s, 500 ms.

**$ArBeN(SiMe_3)_2$ (7).** With stirring, $LiN(SiMe_3)_2$ (0.21 g, 1.25 mmol) was added via a solids-addition tube to a solution of **2** (0.54 g, 1.25 mmol) in *ca.* 15 mL of toluene. Stirring was continued at ambient temperature overnight, whereupon the solvent was removed under reduced pressure. The remaining solid was extracted with *ca.* 20 mL of *n*-hexane, and the extract was filtered over a Celite-padded frit. The volume of the filtrate was reduced to *ca.* 4 mL, and the solution was cooled in a −20 °C freezer to give **7** as colorless crystals. Yield: 0.40 g (66%). Mp: 183−185 °C. $^1$H NMR ($C_6D_6$): $\delta$ −0.08 ($\mathrm{Si(C}H_3)_3$), 2.19 ($o$-$\mathrm{C}H_3$), 2.21 ($p$-$\mathrm{C}H_3$), 6.88 (*m*-Mes), 7.01 (d, $m$- $C_6H_3$), 7.30 (t, $p$-$C_6H_3$). $^{13}$C NMR ($C_6D_6$): $\delta$ 3.6 ($\mathrm{Si(}C\mathrm{H_3)_3}$), 21.0 ($p$-$C\mathrm{H_3}$), 21.5 ($o$-$C\mathrm{H_3}$), 126.5 ($m$-$C_6H_3$), 129.7 ($p$-$C_6H_3$), 128.9 (*m*-Mes), 135.7 (*o*-Mes), 136.6 (*p*-Mes), 142.5 (*i*-Mes), 146.1 ($i$-$C_6H_3$), 151.4 ($o$-$C_6H_3$). $^9$Be NMR ($C_6D_6$, 20 °C [70 °C]): $\delta$ 15.6 [15.7] ($w_{1/2}$ = 580 [230] Hz). IR (Nujol, $cm^{-1}$): 1723 w, 1610 ms, 1568 m, 1541 m, 1511 w, 1394 sh, 1281 sh, 1247 vs, 1171 s, 1160 sh, 1083 s, 1021 s, 932 vs, 879 s, 838 vs, 821 sh, 808 sh, 758 s, 744 s, 735 sh, 681 s, 662 w, 614 w, 550 vw, 471 m, 388 s, 245 m.

**$Ar(THF)_2Be(OC)_3Mo(\eta^5$-$C_5H_5)$·$2C_7H_8$ (8·2 $C_7H_8$).** A solution of $NaMo(\eta^5$-$C_5H_5)(CO)_3$ in *ca.* 50 mL of THF, freshly prepared by sodium amalgam reduction of $(Mo(\eta^5$-$C_5H_5)(CO)_3)_2$ (0.44 g, 0.90 mmol), was added dropwise at *ca.* −78 °C to a solution of **2** (0.78 g, 1.80 mmol) in *ca.* 15 mL of diethyl ether. After warming to room temperature, the red-brown mixture was stirred for 4 h, whereupon the solvent was removed under reduced pressure. The remaining solid was extracted with *ca.* 20 mL toluene, and the extract was filtered. Reduction of the volume of the extract to *ca.* 10 mL and cooling in a −20 °C freezer afforded large red-brown crystals of compound **8**. Yield: 0.84 g (52%). Mp: 46−47 °C. $^1$H NMR ($C_6D_6$): $\delta$ 1.21 (m, $\mathrm{OCH_2C}H_2$), 2.11 ($\mathrm{C_7}H_8$), 2.14 ($o$-$\mathrm{C}H_3$), 2.27 ($p$-$\mathrm{C}H_3$), 3.38 (m, $\mathrm{OC}H_2\mathrm{CH_2}$), 5.29 ($\eta^5$-$C_5H_5$), 6.85 (*m*-Mes), 6.92 (d, $m$- $C_6H_3$), 6.99−7.12 (m, $\mathrm{C_7}H_8$), 7.30 (t, $p$-$C_6H_3$).

$^{13}$C NMR ($C_6D_6$): $\delta$ 21.2 (*p*-$CH_3$), 21.4 ($C_7H_8$), 21.7 (*o*-$CH_3$), 24.8 ($OCH_2CH_2$), 71.0 ($OCH_2CH_2$), 89.2 (Cp), 126.9 (*p*-$C_6H_3$), 127.1 (*m*-$C_6H_3$), 128.2 (*m*-Mes), 135.0 (*p*-Mes), 135.9 (*o*-Mes), 145.1 (*i*-Mes), 150.8 (*o*-$C_6H_3$), 152.8 (*i*-$C_6H_3$), 235.6 (*C*O). $^9$Be NMR ($C_6D_6$, 70 °C): $\delta$ 2.7 ($w_{1/2}$ = 150 Hz). IR (Nujol, cm$^{-1}$): 2011 ms, 1956 sh, 1940 vs, 1847 sh, 1835 s, 1726 m, 1705 m, 1635 ms, 1610 sh, 1300 m, 1164 w, 1142 m, 1113 vw, 1070 w, 1020 m, 940 w br, 886 vw, 848 m, 804 m, 778 m, 724 s, 690 w, 630 vw, 560 w, 488 w, 457 vw, 403 vw.

**$PhC(NSiMe_3)_2(BeCl)_2N(SiMe_3)_2$ (9) and $Be\{(NSiMe_3)_2CPh\}_2$ (10).** Benzonitrile (0.66 mL, 6.3 mmol) was added dropwise to a rapidly stirred solution of $LiN(SiMe_3)_2$ (1.64 g, 9.8 mmol) in *ca*. 30 mL of diethyl ether. After 4 h at ambient temperature, $BeCl_2$ (0.78 g, 9.8 mmol) was added via a solids-addition tube, and stirring was continued overnight. The solvent was removed under reduced pressure, and the remaining solid was extracted with *ca*. 10 mL of dichloromethane. The extract was filtered and stored in a −20 °C freezer to give colorless crystals of compound **9** in 25% yield. All volatile materials were removed from the filtrate, and the remaining solid was redissolved in *ca*. 7 mL of *n*-hexane. Cooling in a −20 °C freezer afforded large colorless crystals of compound **10** in 31% yield. Data for **9** are as follows. Mp: softens >110 °C, melts 171−172 °C. $^1$H NMR ($C_6D_6$): $\delta$ 0.02 ($NSiMe_3$), 0.61 ($N(SiMe_3)_2$), 6.79−6.94 (m, Ph). $^{13}$C NMR ($C_6D_6$): $\delta$ 3.5 ($NSiMe_3$), 4.9 ($N(SiMe_3)_2$), 127.9 (*o*-Ph), 129.5 (*m*-Ph), 130.6 (*o*-Ph), 139.8 (*i*-Ph), 184.1 (*C*Ph). $^9$Be NMR ($C_6D_6$, 70 °C): $\delta$ 11.4 ($w_{1/2}$ = 105 Hz). IR (Nujol, cm$^{-1}$): 1601 w, 1252 vs, 1156 m, 1073 w, 1007 vs, 850 vs br, 773 sh, 761 sh, 744 vs, 719 sh, 702 sh, 680 vs, 602 m, 500 m, 427 m, 330 w. Data for **10** are as follows. Mp: 137−139 °C. $^1$H NMR ($C_6D_6$): $\delta$ 0.12 ($SiMe_3$), 7.04, 7.27 (m, Ph). $^{13}$C NMR ($C_6D_6$): $\delta$ 1.5 ($NSiMe_3$), 126.2 (*o*-Ph), 128.2 (*m*-Ph), 128.7 (*p*-Ph), 140.8 (*i*-Ph), 182.7 (*C*Ph). $^9$Be NMR ($C_6D_6$, 20 °C): $\delta$ 5.5 ($w_{1/2}$ = 6.7 Hz). IR (Nujol, cm$^{-1}$): 1601 vw, 1575 vw, 1306 vw, 1244 vs, 1194 vw, 1113 vw, 1060 w, 1043 m, 1009 s, 995 m, 895 vs br, 840 vs br, 765 s br, 695 s, 602 m, 430 m, 302 ms, 250 w.

**X-ray Crystallographic Studies.** X-ray-quality crystals were obtained as described in the syntheses. Crystals were removed from Schlenk tubes and immediately covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, and instantly placed in a low-temperature $N_2$ stream, as previously described.[8] All data were collected at 130 K (**1**−**9**) or 185 K (**10**) using either a Siemens R3 (**1**, **2a**, **3**, **7**, **8**), a Siemens P4/RA (**2b**, **4**, **6**, **9**, **10**), or a Syntex P2$_1$ (**4**, **5**) diffractometer. Crystal data are given in Table 1. Calculations were carried out with the SHELXTL-PLUS and SHELXL-93 program systems installed on a UNIX workstation or PC's. Scattering factors and the correction for anomalous scattering were taken from common sources.[9] All structures were solved by direct methods and refined by blocked-diagonal least-squares procedures. An absorption correction was applied by using the program XABS2.[10] Anisotropic thermal parameters were included for all non-hydrogen atoms, excluding all C atoms of the disordered phenylamido groups in **5**. Disordered groups in compounds **4** (4-*t*-Bu group), **5** (both phenylamido ligands), **6** (one $OEt_2$ ethyl group), and **8** (solvate toluene) were successfully modeled as described in the Supporting Information. The disordered phenyl rings in **5** and **8** and one phenyl group in **10** were constrained to regular hexagons. Positions and isotropic thermal parameters for H atoms in compounds **7** and **9** and the positions for the H−N hydrogen atoms in **5** and **6** were allowed to refine. All other H atoms were included by use of a riding model with fixed C−H distances and either refined or fixed isotropic thermal parameters equal to 1.2 or 1.5 times that of the bonded carbon. The absolute configuration of compound **5** could not be determined. Final *R* factors are listed in Table 1. Important bond distances and angles are given in Table 2. Further details are provided in the Supporting Information.

## Results and Discussion

Several recent papers have shown that the terphenyl ligands can effect the stabilization of a range of low-coordinate and multiply-bonded compounds which have not yet been shown to be stable with the use of other ligands.[4,11] The extension of terphenyl ligands to a wider range of elements thus offers the prospect that hitherto unknown species with new types of bonding can be isolated. A key feature of the data already published has been the fact that in many instances the terphenyl ligand or ligands have has been sufficiently bulky to stabilize low-coordinate precursors bearing either reactive substituents (e.g., element−halogen bonds) or empty valence orbitals at the central element.[11] In this work the syntheses of several sterically encumbered beryllium derivatives of the $-C_6H_3$-2,6-$Mes_2$ ligand are now described.

The following complexes are of primary interest in this work. The symbol Ar = $-C_6H_3$-2,6-$Mes_2$ is used throughout.

$BeBr_2(OEt_2)_2$ (**1**)
$ArBeCl(OEt_2)$ (**2**)
$ArBeBr(OEt_2)$ (**3**)
$ArBeSMes^*(OEt_2)$ (**4**)
$(ArBeNHPh)_2$ (**5**)
$ArBeNHSiPh_3(OEt_2)$ (**6**)
$ArBeN(SiMe_3)_2$ (**7**)
$Ar(THF)_2Be(OC)_3Mo(\eta^5$-$C_5H_5)$ (**8**)
$PhC(NSiMe_3)_2(BeCl)_2N(SiMe_3)_2$ (**9**)
$Be\{(NSiMe_3)_2CPh\}_2$ (**10**)

**Synthesis.** The arylberyllium halide etherate complexes **2** and **3** were synthesized by the addition of 1 equiv of LiAr (Ar = $-C_6H_3$-2,6-$Mes_2$) to 1 equiv of $BeCl_2$ or $BeBr_2(Et_2O)_2$, **1**, suspended or dissolved in ether. The etherate $BeBr_2(Et_2O)_2$, **1**, was synthesized in *ca*. 80% yield by the treatment of elemental beryllium with $HgBr_2$.[12] Both **2** and **3** were isolated in at least 60% yield, and large crystals of each were obtained from toluene or diethyl ether solution. Further treatment of **2** with LiSMes* afforded the thiolate **4** in moderate yield by simple salt elimination. This compound represents a very rare example of a well-characterized beryllium thiolate complex.[13] The amido derivatives **5**−**7** were obtained by the reaction of the appropriate lithium amide with **2**. The phenylamido derivative $(ArBeNHPh)_2$, **5**, is marked by unusual thermal sensitivity. For instance, the reaction mixture of **2** and LiNHPh affords the arene 1,3-$Mes_2C_6H_4$ in a quantity almost equal to that of the expected product **5**. The product **5** itself appears to be unstable under ambient conditions and decomposes to afford further quantities of 1,3-$Mes_2C_6H_4$ and insoluble material corresponding to the imide $(BeNPh)_x$. The use of more sterically crowding amide substituents $-NHSiPh_3$ and $-N(SiMe_3)_2$ results in the monomeric species **6** and **7** in good yield. In the case of **6**, $Et_2O$ is also coordinated to the beryllium so that a three-coordinate beryllium product is obtained. Increasing the size of the amide to $-N(SiMe_3)_2$ results in the isolation of **7**, which features the first two-coordinate beryllium structurally characterized in the solid state. Reaction of $BeCl_2$ with $Na[Mo(\eta^5$-$C_5H_5)(CO)_3]$ did not afford a Be−Mo bonded species. Instead, the red isocarbonyl complex **8** was obtained in high yield. The reaction of $BeCl_2$ with the amidinate $Li(NSiMe_3)_2CPh$[14] formed from the reaction of $LiN(SiMe_3)_2$ with PhCN gave compounds **9** and **10**. It was originally intended to synthesize the monomeric species $ClBe(NSiMe_3)_2CPh$ via a reaction of a 1:1:1 mixture of PhCN, $LiN(SiMe_3)_2$, and $BeCl_2$. In a fortuitous

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**Table 1.** Selected Crystallographic Data for **1**−**10**[a]

| | **1** | **2a** | **2b** | **3** | **4**·0.5$C_6H_{14}$ | **5**·$C_4H_{10}O$ |
|---|---|---|---|---|---|---|
| empirical formula | $C_8H_{10}BeBr_2O_2$ | $C_{28}H_{35}BeClO$ | $C_{28}H_{35}BeClO$ | $C_{28}H_{35}BeBrO$ | $C_{49}H_{71}BeOS$ | $C_{76}H_{72}Be_2N_2O$ |
| fw | 317.1 | 432.0 | 432.0 | 476.5 | 717.1 | 903.3 |
| color, habit | colorless, block | colorless, block | colorless, block | colorless, block | colorless, plate | colorless, block |
| crystal system | monoclinic | orthorhombic | triclinic | triclinic | triclinic | monoclinic |
| space group | $P2_1/n$ | Pbca | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ | $P2_1$ |
| a/Å | 11.690(5) | 13.136(3) | 8.857(1) | 8.873(5) | 9.732(1) | 11.894(2) |
| b/Å | 10.191(3) | 13.877(3) | 8.8977(9) | 8.847(5) | 11.190(1) | 12.212(2) |
| c/Å | 12.131(5) | 28.092(6) | 18.198(2) | 18.251(7) | 21.841(2) | 18.709(3) |
| α/deg | | | 86.437(8) | 86.54(4) | 75.225(7) | |
| $\beta$/deg | 114.67(3) | | 82.677(8) | 83.17(4) | 81.137(8) | 99.24(1) |
| $\gamma$/deg | | | 62.405(7) | 64.14(4) | 73.382(8) | |
| $V$/Å$^3$ | 1313.3(9) | 5121(2) | 1260.5(2) | 1280(1) | 2195.3(4) | 2682.4(7) |
| $Z$ | 4 | 8 | 2 | 2 | 2 | 2 |
| $d$/g·cm$^{-3}$ | 1.604 | 1.121 | 1.138 | 1.236 | 1.085 | 1.118 |
| cryst dimens/mm | 0.50 × 0.44 × 0.40 | 0.64 × 0.30 × 0.20 | 0.64 × 0.48 × 0.26 | 0.70 × 0.42 × 0.20 | 1.20 × 1.00 × 0.16 | 0.72 × 0.60 × 0.32 |
| $\mu$/cm$^{-1}$ | 61.44 | 1.65 | 11.38 | 16.22 | 8.88 | 4.83 |
| no. of unique data | 3497 | 3996 | 3337 | 5603 | 5935 | 4624 |
| no. of data with $I > 2\sigma(I)$ | 2269 | 2321 | 3125 | 3809 | 5271 | 4415 |
| no. of parameters | 142 | 321 | 323 | 318 | 588 | 606 |
| $R_1$ ($I > 2\sigma(I)$) | 0.0619 | 0.0581 | 0.0477 | 0.0705 | 0.0615 | 0.0445 |
| w$R_2$ (all data) | 0.1471 | 0.1276 | 0.1308 | 0.1896 | 0.1702 | 0.1166 |

| | **6** | **7** | **8**·2$C_7H_8$ | **9** | **10** |
|---|---|---|---|---|---|
| empirical formula | $C_{46}H_{51}BeNOSi$ | $C_{30}H_{43}BeNSi_2$ | $C_{54}H_{62}BeMoO_5$ | $C_{19}H_{41}Be_2Cl_2N_3Si_4$ | $C_{26}H_{46}BeN_4Si_4$ |
| fw | 671.0 | 482.8 | 896.0 | 512.8 | 536.0 |
| color, habit | colorless, block | colorless, plate | wine red, block | colorless, plate | colorless, block |
| crystal system | monoclinic | orthorhombic | monoclinic | orthorhombic | monoclinic |
| space group | $P2_1/c$ | Pbcn | $P2_1/c$ | Pbca | $P2_1/c$ |
| $a$/Å | 11.959(2) | 12.623(3) | 19.111(4) | 19.996(4) | 20.022(2) |
| $b$/Å | 16.655(2) | 15.404(4) | 11.976(3) | 14.816(2) | 9.7161(9) |
| $c$/Å | 19.718(2) | 15.502(3) | 21.241(5) | 20.183(4) | 19.456(2) |
| α/deg | | | | | |
| $\beta$/deg | 105.368(9) | | 103.47(2) | | 111.392(8) |
| $\gamma$/deg | | | | | |
| $V$/Å$^3$ | 3786.9(8) | 3014(1) | 4728(2) | 5979(2) | 3524.1(6) |
| $Z$ | 4 | 4 | 4 | 8 | 4 |
| $d$/g·cm$^{-3}$ | 1.177 | 1.064 | 1.259 | 1.139 | 1.010 |
| cryst dimens/mm | 0.30 × 0.18 × 0.18 | 0.64 × 0.60 × 0.10 | 0.80 × 0.36 × 0.30 | 0.50 × 0.46 × 0.10 | 0.56 × 0.34 × 0.20 |
| $\mu$/cm$^{-1}$ | 8.06 | 1.35 | 3.24 | 35.65 | 16.98 |
| no. of unique data | 4931 | 3123 | 8346 | 3908 | 4631 |
| no. of data with $I > 2\sigma(I)$ | 4086 | 2342 | 5590 | 3064 | 3409 |
| no. of params | 537 | 242 | 644 | 435 | 316 |
| $R_1$ ($I > 2\sigma(I)$) | 0.0474 | 0.0461 | 0.0485 | 0.0432 | 0.0751 |
| w$R_2$ (all data) | 0.1318 | 0.1226 | 0.1129 | 0.1113 | 0.2287 |

[a] All data were collected at 130 K (**1**−**9**) or 88 K (**10**) with Mo Kα ($\lambda$ = 0.710 73 Å) (**1**, **2a**, **3**, **7**, **8**) or Cu Kα ($\lambda$ = 1.541 78 Å) (**2b**, **4**−**6**, **9**, **10**) radiation.

manner, only approximately half the requisite amount of PhCN was utilized in the synthesis so that the product **9**, which may be considered a 1:1 mixture of the compounds $ClBe(NSiMe_3)_2CPh$ and $ClBeN(SiMe_3)_2$, was isolated.

**Structures.** Compounds **1**−**10** were characterized by X-ray crystallography. The structure of **1** (Figure 1) appears to be the first full structural determination of a beryllium dibromide species.[15] Oddly, crystals of **1** are not isomorphous with those of $BeCl_2(Et_2O)_2$,[13,16] although the structures are broadly similar, being composed of monomeric molecules with a distorted tetrahedral geometry at beryllium. The Be−Br distances, average 2.173(8) Å, are *ca*. 0.2 Å longer than the 1.978(3) Å observed for the Be−Cl bond in $BeCl_2(Et_2O)_2$. This distance is somewhat greater than that expected on the basis of the difference (0.145 Å) in covalent radii[17] between Cl (0.99 Å) and Br (1.135 Å). If, however, allowance is made for the ionic character[18] of the Be−Br bond, a Be−Br distance of 2.14 Å may be estimated, which is in reasonable agreement with the experimental value. Nonetheless, the Be−Br distance in **1** is the longest of the three measured to date: a distance of 2.122(7) Å was measured in {$\eta^3$-HB(3-*t*-Bupz)$_3$}BeBr[19] and a distance of 1.943(15) Å was observed in the gas phase electron diffraction study of $\eta^5$-$C_5H_5$BeBr.[20] The average Be−O distance, 1.656(9) Å is marginally shorter than that observed (1.683(3) Å) in $BeCl_2(Et_2O)_2$.[13]

The arylberyllium halide compounds **2** and **3**, which are the first structurally characterized beryllium Grignard analogues, have quite similar structures (Figures 2 and 3). Depending on the solvent used, the compound **2** could be crystallized in two different space groups (designated as compounds **2a** and **2b**, **2b** being isomorphous with **3**). The crystal structures of **2a** and **2b** revealed differences of up to *ca*. 0.04 Å and *ca*. 5° in corresponding bond distances and angles. Both compounds are

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**Table 2.** Selected Bond Distances (Å) and Angles (deg) for **1**−**10**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Complex **1** | | | | | | | |
| Be(1)−Br(1) | 2.176(8) | Be(1)−O(1) | 1.648(9) | O(1)−C(3) | 1.449(7) | O(2)−C(6) | 1.458(7) |
| Be(1)−Br(2) | 2.170(8) | Be(1)−O(2) | 1.664(9) | O(1)−C(2) | 1.468(7) | O(2)−C(7) | 1.461(7) |
| O(1)−Be(1)−O(2) | 103.3(5) | O(2)−Be(1)−Br(2) | 109.2(4) | O(2)−Be(1)−Br(1) | 110.1(4) | Br(2)−Be(1)−Br(1) | 111.6(4) |
| O(1)−Be(1)−Br(2) | 112.2(5) | O(1)−Be(1)−Br(1) | 110.2(4) | | | | |
| Complex **2a** | | | | | | | |
| Be(1)−C(1) | 1.740(6) | Be(1)−O(1) | 1.612(5) | O(1)−C(27) | 1.463(4) | C(1)−C(6) | 1.410(4) |
| Be(1)−Cl(1) | 1.946(5) | O(1)−C(26) | 1.476(4) | C(1)−C(2) | 1.412(4) | | |
| O(1)−Be(1)−C(1) | 122.2(3) | C(2)−C(1)−C(6) | 116.1(3) | Be(1)−C(1)−C(6) | 119.7(3) | Be(1)−O(1)−C(26) | 123.8(3) |
| O(1)−Be(1)−Cl(1) | 111.8(3) | Be(1)−C(1)−C(2) | 124.2(3) | C(26)−O(1)−C(27) | 113.4(3) | Be(1)−O(1)−C(27) | 122.2(3) |
| C(1)−Be(1)−Cl(1) | 126.0(3) | | | | | | |
| Complex **2b** | | | | | | | |
| Be(1)−C(1) | 1.783(4) | Be(1)−O(1) | 1.604(3) | O(1)−C(27) | 1.463(3) | C(1)−C(6) | 1.415(3) |
| Be(1)−Cl(1) | 1.905(3) | O(1)−C(26) | 1.466(3) | C(1)−C(2) | 1.406(3) | | |
| O(1)−Be(1)−C(1) | 116.5(2) | C(2)−C(1)−C(6) | 116.7(2) | Be(1)−C(1)−C(6) | 119.4(2) | Be(1)−O(1)−C(26) | 121.9(2) |
| O(1)−Be(1)−Cl(1) | 114.0(2) | Be(1)−C(1)−C(2) | 123.9(2) | C(26)−O(1)−C(27) | 113.9(2) | Be(1)−O(1)−C(27) | 123.8(2) |
| C(1)−Be(1)−Cl(1) | 129.3(2) | | | | | | |
| Complex **3** | | | | | | | |
| Be(1)−C(1) | 1.749(7) | Be(1)−O(1) | 1.612(7) | O(1)−C(27) | 1.467(6) | C(1)−C(6) | 1.407(6) |
| Be(1)−Br(1) | 2.071(6) | O(1)−C(26) | 1.468(6) | C(1)−C(2) | 1.412(6) | | |
| O(1)−Be(1)−C(1) | 117.9(4) | C(2)−C(1)−C(6) | 116.6(4) | Be(1)−C(1)−C(6) | 119.4(4) | Be(1)−O(1)−C(26) | 124.0(4) |
| O(1)−Be(1)−Br(1) | 112.3 | Be(1)−C(1)−C(2) | 124.0(4) | C(26)−O(1)−C(27) | 113.2(4) | Be(1)−O(1)−C(27) | 122.6(3) |
| C(1)−Be(1)−Br(1) | 129.7(4) | | | | | | |
| Complex **4**·0.5$C_6H_{14}$ | | | | | | | |
| Be(1)−C(1) | 1.762(4) | Be(1)−O(1) | 1.621(4) | O(1)−C(44) | 1.471(3) | O(1)−C(45) | 1.463(3) |
| Be(1)−S(1) | 1.984(3) | S(1)−C(25) | 1.810(3) | | | | |
| O(1)−Be(1)−C(1) | 117.8(2) | C(44)−O(1)−C(45) | 115.0(2) | Be(1)−C(1)−C(2) | 123.9(2) | C(26)−C(25)−C(30) | 119.6(2) |
| O(1)−Be(1)−S(1) | 121.7(2) | Be(1)−O(1)−C(45) | 121.1(2) | Be(1)−C(1)−C(6) | 120.6(2) | C(26)−C(25)−S(1) | 119.7(2) |
| C(1)−Be(1)−S(1) | 120.5(2) | Be(1)−O(1)−C(44) | 123.8(2) | C(1)−C(2)−C(7) | 123.3(2) | C(30)−C(25)−S(1) | 120.8(2) |
| C(25)−S(1)−Be(1) | 116.17(13) | C(2)−C(1)−C(6) | 115.5(2) | C(1)−C(6)−C(16) | 120.5(2) | | |
| Complex **5**·$C_4H_{10}O$ | | | | | | | |
| Be(1)−C(1) | 1.733(5) | Be(1)−N(2) | 1.701(6) | Be(1)−Be(2) | 2.303(6) | N(1)−H(1) | 1.08(6) |
| Be(2)−C(25) | 1.734(5) | Be(2)−N(1) | 1.725(6) | N(1)−C(49) | 1.450(5) | N(2)−H(2) | 1.92(6) |
| Be(1)−N(1) | 1.690(6) | Be(2)−N(2) | 1.724(5) | N(2)−C(55) | 1.457(5) | | |
| N(1)−Be(1)−N(2) | 96.4(3) | C(49)−N(1)−Be(2) | 118.0(4) | Be(1)−N(2)−H(2) | 113(4) | C(26)−C(25)−Be(2) | 121.8(3) |
| N(1)−Be(1)−C(1) | 133.8(3) | C(49)−N(1)−H(1) | 113(3) | Be(2)−N(2)−H(2) | 113(4) | C(30)−C(25)−Be(2) | 121.9(2) |
| N(2)−Be(1)−C(1) | 129.8(3) | Be(1)−N(1)−H(1) | 111(3) | C(2)−C(1)−C(6) | 116.3(3) | C(25)−C(26)−C(31) | 119.3(3) |
| N(2)−Be(2)−N(1) | 94.2(3) | Be(2)−N(1)−H(1) | 113(3) | C(6)−C(1)−Be(1) | 122.1(2) | C(25)−C(30)−C(40) | 120.1(3) |
| N(1)−Be(2)−C(25) | 13.60(3) | Be(1)−N(2)−Be(2) | 84.5(3) | C(2)−C(1)−Be(1) | 121.5(3) | C(50)−C(49)−N(1) | 117.2(3) |
| N(2)−Be(2)−C(25) | 129.7(3) | C(55)−N(2)−Be(1) | 116.1(4) | C(1)−C(2)−C(7) | 121.0(3) | C(54)−C(49)−N(1) | 122.8(3) |
| Be(1)−N(1)−Be(2) | 84.8(3) | C(55)−N(2)−Be(2) | 115.9(3) | C(1)−C(6)−C(16) | 119.4(3) | C(56)−C(55)−N(2) | 117.3(3) |
| C(49)−N(1)−Be(1) | 115.1(3) | C(55)−N(2)−H(2) | 111(3) | C(26)−C(25)−C(30) | 116.2(3) | C(60)−C(55)−N(2) | 122.7(3) |
| Complex **6** | | | | | | | |
| Be(1)−C(1) | 1.780(4) | N(1)−Si(1) | 1.703(2) | O(1)−C(45) | 1.465(9) | Si(1)−C(31) | 1.886(3) |
| Be(1)−N(1) | 1.577(4) | N(1)−H(1) | 0.81(3) | Si(1)−C(25) | 1.881(3) | Si(1)−C(37) | 1.887(3) |
| Be(1)−O(1) | 1.655(4) | O(1)−C(44) | 1.462(3) | | | | |
| N(1)−Be(1)−O(1) | 113.7(2) | Be(1)−N(1)−H(1) | 109.8(23) | Be(1)−O(1)−C(45) | 118.8(4) | Be(1)−C(1)−C(6) | 122.2(2) |
| N(1)−Be(1)−C(1) | 131.2(2) | Si(1)−N(1)−H(1) | 109.9(22) | C(2)−C(1)−C(6) | 115.1(2) | C(1)−C(2)−C(7) | 120.8(2) |
| O(1)−Be(1)−C(1) | 115.1(2) | C(44)−O(1)−C(45) | 114.1(4) | Be(1)−C(1)−C(2) | 122.7(2) | C(1)−C(6)−C(16) | 119.8(2) |
| Be(1)−N(1)−Si(1) | 134.6(2) | Be(1)−O(1)−C(44) | 123.1(2) | | | | |
| Complex **7** | | | | | | | |
| Be(1)−C(1) | 1.700(4) | N(1)−Si(1) | 1.7326(11) | Si(1)−C(15) | 1.863(3) | Si(1)−C(16) | 1.864(3) |
| Be(1)−N(1) | 1.519(4) | Si(1)−C(14) | 1.860(3) | | | | |
| N(1)−Be(1)−C(1) | 180.0 | N(1)−Si(1)−C(14) | 108.72(12) | N(1)−Si(1)−C(16) | 112.03(11) | Be(1)−C(1)−C(2) | 121.14(11) |
| Be(1)−N(1)−Si(1) | 118.43(6) | N(1)−Si(1)−C(15) | 110.77(10) | C(2)−C(1)−C(2)′ | 117.7(2) | C(1)−C(2)−C(5) | 118.1(2) |
| Si(1)−N(1)−Si(1)′ | 123.14(12) | | | | | | |
| Complex **8**·$C_7H_8$ | | | | | | | |
| Be(1)−C(1) | 1.782(5) | Mo(1)−C(34) | 1.946(4) | Mo(1)−C(39) | 2.374(4) | O(2)−C(29) | 1.466(4) |
| Be(1)−O(1) | 1.718(5) | Mo(1)−C(35) | 1.949(5) | Mo(1)−C(40) | 2.376(4) | O(3)−C(33) | 1.212(4) |
| Be(1)−O(2) | 1.682(5) | Mo(1)−C(36) | 2.361(4) | O(1)−C(28) | 1.459(4) | O(4)−C(34) | 1.157(5) |
| Be(1)−O(3) | 1.657(5) | Mo(1)−C(37) | 2.358(5) | O(1)−C(25) | 1.466(5) | O(5)−C(35) | 1.163(5) |
| Mo(1)−C(33) | 1.875(3) | Mo(1)−C(38) | 2.372(4) | O(2)−C(32) | 1.459(4) | | |

**Table 2** (Continued)

Complex **8**·$C_7H_8$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| O(1)−Be(1)−O(3) | 99.6(3) | C(33)−Mo(1)−C(34) | 89.1(2) | C(29)−O(2)−C(32) | 110.5(3) | Be(1)−C(1)−C(6) | 126.8(3) |
| O(1)−Be(1)−O(2) | 102.0(3) | C(33)−Mo(1)−C(35) | 86.9(2) | Be(1)−O(2)−C(29) | 124.4(3) | C(1)−C(2)−C(7) | 122.1(3) |
| O(2)−Be(1)−O(3) | 104.4(3) | C(34)−Mo(1)−C(35) | 88.7(2) | Be(1)−O(2)−C(32) | 125.1(3) | C(1)−C(6)−C(16) | 121.5(3) |
| O(3)−Be(1)−C(1) | 116.0(3) | C(25)−O(1)−C(28) | 109.4(3) | Be(1)−O(3)−C(33) | 147.1(3) | O(3)−C(33)−Mo(1) | 179.1(3) |
| O(2)−Be(1)−C(1) | 111.4(3) | Be(1)−O(1)−C(28) | 125.1(3) | C(2)−C(1)−C(6) | 114.4(3) | O(4)−C(34)−Mo(1) | 176.0(3) |
| O(1)−Be(1)−C(1) | 121.2(3) | Be(1)−O(1)−C(25) | 125.0(3) | Be(1)−C(1)−C(2) | 118.6(3) | O(5)−C(35)−Mo(1) | 179.4(3) |

Complex **9**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Be(1)−Cl(1) | 1.914(5) | Be(1)−O(1)−C(25) | 1.340(4) | Si(1)−C(9) | 1.854(5) | Si(3)−C(15) | 1.859(4) |
| Be(2)−Cl(2) | 1.926(4) | N(2)−C(1) | 1.346(4) | Si(1)−C(10) | 1.858(5) | Si(3)−C(16) | 1.847(4) |
| Be(1)−N(1) | 1.649(6) | N(1)−Si(1) | 1.799(3) | Si(2)−C(11) | 1.853(4) | Si(4)−C(17) | 1.863(4) |
| Be(2)−N(2) | 1.651(6) | N(2)−Si(2) | 1.787(3) | Si(2)−C(12) | 1.859(4) | Si(4)−C(18) | 1.866(4) |
| Be(1)−N(3) | 1.686(5) | N(3)−Si(3) | 1.790(3) | Si(2)−C(13) | 1.866(5) | Si(4)−C(19) | 1.850(5) |
| Be(2)−N(3) | 1.671(5) | N(3)−Si(4) | 1.803(3) | Si(3)−C(14) | 1.866(4) | C(1)−C(2) | 1.494(5) |
| Be(1)--Be(2) | 2.567(6) | Si(1)−C(8) | 1.855(5) | | | | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| N(1)−Be(1)−N(3) | 119.6(3) | C(1)−N(1)−Be(1) | 117.2(3) | Be(2)−N(2)−Si(2) | 118.4(2) | Be(1)−N(3)−Si(4) | 109.2(2) |
| N(1)−Be(1)−Cl(1) | 116.6(3) | C(1)−N(1)−Si(1) | 125.1(3) | Be(2)−N(3)−Be(1) | 99.7(3) | Si(3)−N(3)−Si(4) | 116.9(2) |
| N(3)−Be(1)−Cl(1) | 123.7(3) | Be(1)−N(1)−Si(1) | 117.492) | Be(2)−N(3)−Si(3) | 110.1(2) | N(1)−C(1)−N(2) | 121.8(3) |
| N(2)−Be(2)−N(3) | 121.1(3) | C(1)−N(2)−Be(2) | 116.5(3) | Be(1)−N(3)−Si(3) | 109.4(2) | N(1)−C(1)−C(2) | 118.7(3) |
| N(2)−Be(2)−Cl(2) | 116.9(3) | C(1)−N(2)−Si(2) | 124.9(2) | Be(2)−N(3)−Si(4) | 110.1(2) | N(2)−C(1)−C(2) | 119.5(3) |
| N(3)−Be(2)−Cl(2) | 122.0(3) | | | | | | |

Complex **10**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Be−C(1) | 2.063(7) | Si(2)−N(2) | 1.715(3) | Si(2)−C(12) | 1.847(7) | Si(4)−C(26) | 1.809(7) |
| Be−C(14) | 2.065(7) | Si(3)−N(3) | 1.716(3) | Si(2)−C(13) | 1.837(7) | N(1)−C(1) | 1.329(5) |
| Be−N(1) | 1.729(6) | Si(4)−N(4) | 1.715(4) | Si(3)−C(21) | 1.833(6) | N(2)−C(1) | 1.332(5) |
| Be−N(2) | 1.730(6) | Si(1)−C(8) | 1.816(7) | Si(3)−C(22) | 1.891(7) | N(3)−C(14) | 1.328(5) |
| Be−N(3) | 1.723(6) | Si(1)−C(9) | 1.854(8) | Si(3)−C(23) | 1.846(7) | N(4)−C(14) | 1.331(5) |
| Be−N(4) | 1.724(7) | Si(1)−C(10) | 1.842(7) | Si(4)−C(24) | 1.849(10) | C(1)−C(2) | 1.486(5) |
| Si(1)−N(1) | 1.707(4) | Si(2)−C(11) | 1.811(8) | Si(4)−C(25) | 1.816(9) | C(14)−C(15) | 1.488(6) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| N(3)−Be−N(4) | 79.6(3) | C(1)−N(1)−Si(1) | 135.0(3) | C(14)−N(3)−Si(3) | 134.5(3) | N(1)−C(1)−N(2) | 112.9(3) |
| N(3)−Be−N(1) | 123.9(4) | C(1)−N(1)−Be | 83.8(3) | C(14)−N(3)−Be | 84.1(3) | N(1)−C(1)−C(2) | 123.2(4) |
| N(4)−Be−N(1) | 124.6(4) | Si(1)−N(1)−Be | 141.2(3) | Si(3)−N(3)−Be | 140.5(3) | N(2)−C(1)−C(2) | 123.9(3) |
| N(3)−Be−N(2) | 128.5(4) | C(1)−N(2)−Si(2) | 134.1(3) | C(14)−N(4)−Si(4) | 135.1(3) | N(3)−C(14)−N(4) | 112.1(4) |
| N(4)−Be−N(2) | 127.4(4) | C(1)−N(2)−Be | 83.6(3) | C(14)−N(4)−Be | 84.0(3) | N(3)−C(14)−C(15) | 124.4(4) |
| N(1)−Be−N(2) | 79.7(3) | Si(2)−N(2)−Be | 142.0(3) | Si(4)−N(4)−Be | 140.8(3) | N(4)−C(14)−C(15) | 123.5(4) |

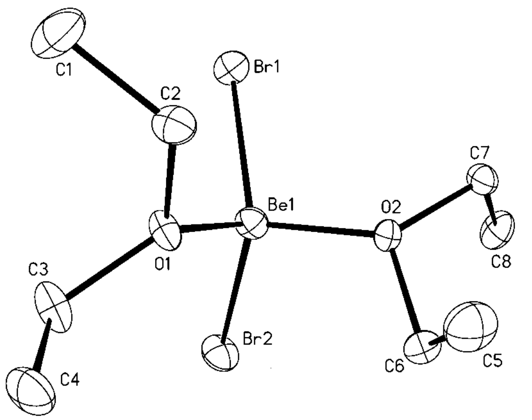

**Figure 1.** Thermal ellipsoid (30%) drawing of **1**. H atoms are not shown.

characterized by a planar three-coordinate geometry at beryllium which is bound to carbon, oxygen, and chlorine ligand atoms. The monomeric formulas of **2** and **3** may be contrasted with the halide-bridged dimeric structure of the related magnesium Grignard derivative {Ar(THF)Mg($\mu$-Br)}$_2$.[21] There is an almost perpendicular orientation of the coordination plane at beryllium with respect to the plane of beryllium-bound aryl group in the three structures. The Be−C distances 1.740(6) and 1.783(4) Å of **2a** and **2b** are close to that (1.739(3) Å) observed for BeMes$_2$(OEt$_2$)[13] and shorter than those observed in the anionic species LiBe($t$-Bu)$_3$.[22] The average Be−O and Be−Cl bond lengths 1.608(5) and 1.926(5) Å are 0.05−0.08 Å shorter than those seen in BeCl$_2$(OEt$_2$)$_2$. This is probably a result of the lower coordination number of the beryllium in **2a** and **2b**. The Be−C and Be−O distances in **3** are very similar to those in **2a** and **2b**, and the Be−Br distance of 2.071(6) Å is 0.1 Å shorter than those observed in **1**, as a result of the lower coordination number of beryllium. Apparently, **2** and **3** are the first compounds to display bonding between three-coordinate beryllium and halogen atoms in the solid state.

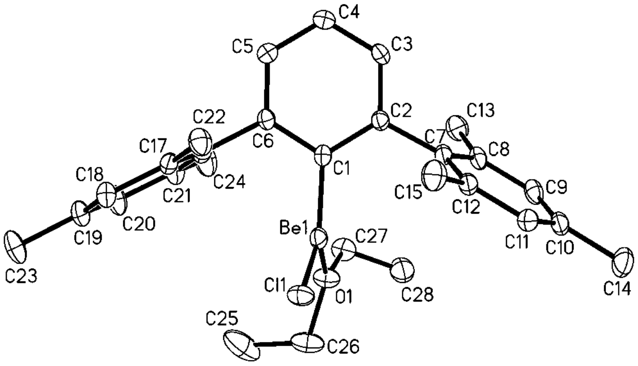

**Figure 2.** Thermal ellipsoid (30%) drawing of **2a**. H atoms are not shown.

The presence of a reactive beryllium−halogen bond in **2** or **3** permits ready derivatization with a variety of lithium reagents. Thus, reaction with 1 equiv of LiSMes* affords the thiolate **4** (Figure 4), which also features three-coordinate beryllium. The Be−S distance 1.984(3) Å is very similar to the 1.989(8) Å

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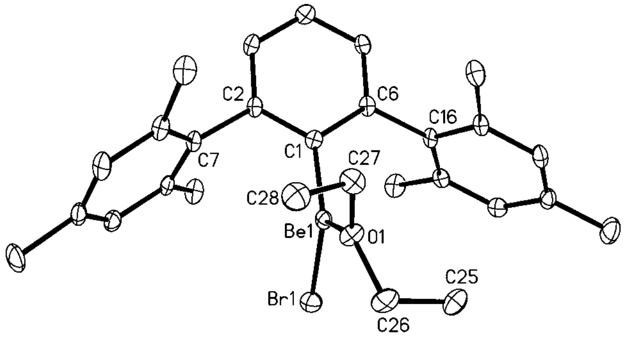

**Figure 3.** Thermal ellipsoid (30%) drawing of **3**. H atoms are not shown.

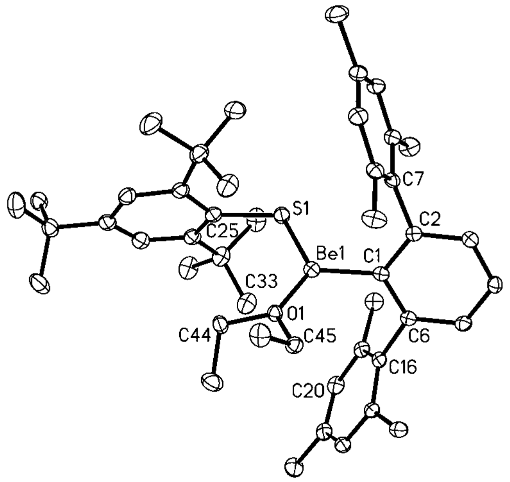

**Figure 4.** Thermal ellipsoid (30%) drawing of **4**. H atoms are not shown.

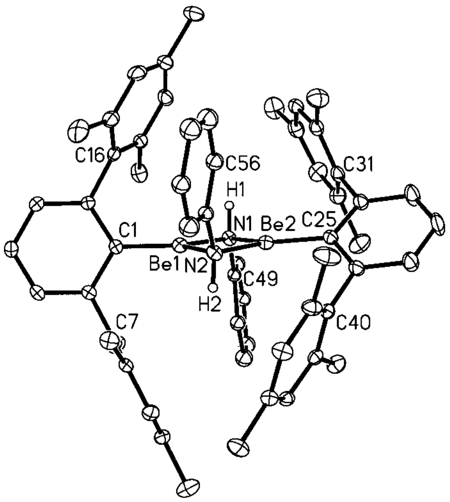

**Figure 5.** Thermal ellipsoid (30%) drawing of **5**. H atoms except those of NH's are not shown.

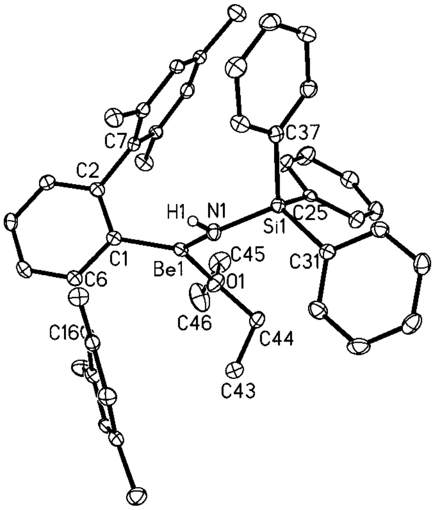

**Figure 6.** Thermal ellipsoid (30%) drawing of **6**. H atoms (except NH) are not shown.

observed in Be(SMes*)$_2$(THF).[13] The Be−C and Be−O bond lengths are comparable to those seen in **2** and **3**. There is a very small angle between the perpendicular to the coordination plane at beryllium and the perpendicular to the plane defined by the Be, S, and C atoms. In addition, the Be−S−C angle, 116.17(13)°, is *ca*. 10° wider than the Be−S−C angles in Be(SMes*)$_2$THF.[13] A relatively close approach (C(20)−C(33) = 3.343 Å) is observed between two carbon atoms of the Ar and Mes* moieties. These structural features point to considerable steric crowding at beryllium rather than the presence of multiple character in the Be−S bond.

The amide derivatives **5**−**7** were synthesized by the reaction of 1 equiv of the appropriate lithium reagent with **2**. Reaction with LNHPh leads to the dimeric product (ArBeNHPh)$_2$ (**5**) (Figure 5), which has an essentially planar Be$_2$N$_2$ core with the amide groups disposed in a *trans* orientation. The Be$_2$N$_2$ ring has internal angles near 95° at beryllium and near 85° at nitrogen. Since the beryllium-coordinated ether in the starting material has been eliminated, the berylliums are both three-coordinate in the product and the Be−C distances are very similar to those observed in **2**−**4**. The Be−N distances are in the range 1.690(6)−1.725(6) Å which is rather longer than the 1.653(7) Å observed for the Be(3-coord)−N (4-coord) distance in {Be(NMe$_2$)$_2$}$_3$[23a] and much longer than the 1.550(4) Å observed for the Be(3-coord)−N(3-coord) distance in the dimer {BeN(Me)SiMe$_2$CH$_2$SiMe$_2$NMe}$_2$.[23b] It is, however, shorter than Be(4-coord)−N(4-coord) bond lengths of 1.785(4) Å in {Be(NMe$_2$)$_2$}$_3$ and 1.747(3) Å in {HBeN(Me)(CH$_2$)$_2$NMe$_2$}$_2$.[23c] Increasing the size of the nitrogen substituent from −Ph to −SiPh$_3$ affords the monomeric compound **6** (Figure 6) by the reaction of LiNHSiPh$_3$ with **2**. The beryllium remains complexed to ether, however, so that a planar three-coordinate beryllium product is obtained. The widest interligand angle (131.2(2)°) at beryllium is between the amide and aryl groups, consistent with the large size of these substituents. The Be−C and Be−O distances are similar to those observed in **2**−**4**. The Be−N distance 1.577(4) Å is very similar to those observed for Be(3-coord)−N(3-coord) in {Be(NMe$_2$)$_2$}$_3$[23a] (1.573(11) Å) and the 1.562(24) Å observed in the vapor phase structure of Be{N(SiMe$_3$)$_2$}$_2$, which features two-coordinate beryllium.[24] The Be−N distance in **6** is far shorter than the sum (1.82 Å) of the standard covalent radii of beryllium (1.12 Å) and nitrogen (sp$^2$ hybridized, 0.70 Å).[25] Even when allowance is made for an ionic correction,[18] a Be−N distance of 1.68 Å is calculated. The significantly lower Be−N bond length in **6** suggests the existence of some $\pi$-bonding between beryllium and nitrogen. The moderate torsion angle (30.5°) between the beryllium and nitrogen coordination planes is consistent with this view.

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(25) The effective radii for atoms in different states of hybridization are discussed in: Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 221.

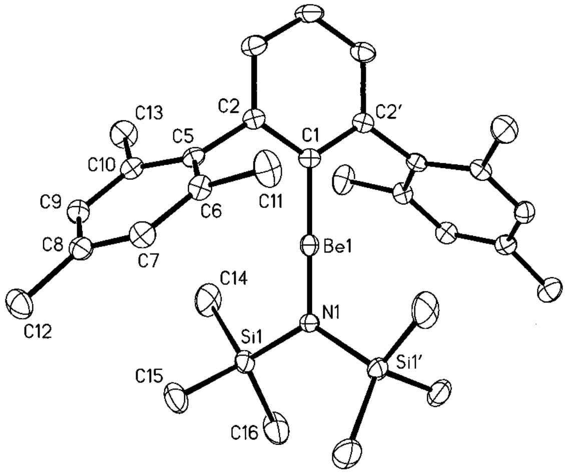

**Figure 7.** Thermal ellipsoid (30%) drawing of **7**. H atoms are not shown.

A further increase in the size of the amide substituent to $-N(SiMe_3)_2$ results in the monomeric product $ArBeN(SiMe_3)_2$, **7** (Figure 7), which features two-coordinate beryllium. The structure has a crystallographically required 2-fold symmetry element along the C−Be−N axis, thereby affording exactly linear coordination at beryllium. The structure of **7** is the first for a two-coordinate beryllium species in the solid state. Although there have been a number of prior reports of structures of two-coordinate beryllium species, all of them have been obtained in the vapor phase. Thus, the aforementioned $Be\{N(SiMe_3)_2\}_2$[24] species is a linear monomer in the vapor phase with mutually perpendicular nitrogen coordination planes, suggesting an isolobal analogy with allene and the possible existence of Be−N $\pi$-bonding. Both $BeMe_2$[26a] and Be(*t*-Bu)$_2$[26b] also have linear, two-coordinate structures in the vapor phase with essentially identical Be−C distances of 1.698(5) and 1.699(3) Å. The Be−C bond length in **7**, 1.700(4) Å, is within one standard deviation of both values. The consistency of these three distances permits the effective covalent radius of beryllium in two-coordinate compounds to be estimated by substitution in the Schomaker−Stevenson formula.[18] Thus, using the experimentally determined value of 1.70 Å as the Be−C bond length, 0.74 Å as a radius of sp$^2$-hybridized carbon, and 0.093 Å as the ionic correction factor, a value of *ca.* 1.05 Å may be estimated for the covalent radius of beryllium in two-coordinate compounds. Addition of 0.7 Å (sp$^2$ covalent radius of nitrogen)[25] to this value affords a predicted value of 1.75 Å for the Be−N single bond in two-coordinate beryllium amide derivatives. Since a Be−N bond has considerable ionic character, the ionic Schomaker−Stevenson correction of 0.13 Å is quite substantial and, when subtracted from 1.75 Å, affords a predicted value of 1.62 Å for the Be−N bond. Since this is *ca.* 0.1 Å longer than the observed bond length of 1.519(4) Å in **7**, the data suggest that Be−N $\pi$-bonding may be present. Incidentally, the Be−N bond length in **7** is the shortest that has been reported to date. The somewhat longer Be−N bond in $Be\{N(SiMe_3)_2\}_2$ suggests that in **7** the Be−N $\pi$-bonding may be enhanced owing to the lack of any competitive $\pi$-interaction with the second nitrogen atom.

The reaction of **2** with NaMo($\eta^5$-$C_5H_5$)(CO)$_3$ was performed with the objective of isolating a transition metal−beryllium species with unusual bonding. The recent reaction[11c] of NaMo($\eta^5$-$C_5H_5$)(CO)$_3$ with Ge(Cl)Ar to give the triply bonded species ($\eta^5$-$C_5H_5$)(CO)$_2$MoGeAr suggested that a similar reaction of an Ar-substituted beryllium halide precursor might afford an unusual product. The isocarbonyl species Ar(THF)$_2$Be(OC)$_3$Mo($\eta^5$-$C_5H_5$) (Figure 8) was isolated from the reaction mixture in good yield. It features a four-coordinate beryllium bound to the aryl group, two THF donors, and an oxygen from one of the molybdenum-bound carbonyls. The coordination at beryllium is distorted tetrahedral. The Be−C distance is marginally longer than the Be−C distances in most of the three-coordinate species although it is virtually the same length as the Be−C bond lengths in **2b** and **6**. The Be−O(THF) bond lengths 1.718(5) and 1.682(5) Å are significantly longer than those in the three-coordinate etherate complexes **2**−**4** and **6** but comparable to those in other four-coordinate beryllium−etherate complexes.[13,16] The Be−O(OC) isocarbonyl interaction has no precedent in beryllium chemistry. The Be−O distance, 1.657(5) Å, is comparable to (and slightly shorter than) the Be−O(THF) distances in the same molecule. It is notable that the O(3)−C(33) distance in the beryllium-bound isocarbonyl, 1.212(4) Å, is *ca.* 0.05 Å (10 standard deviations) longer than those in the other carbonyl ligands. By the same token, the Mo−C(33) length 1.875(3) Å is shorter than the Mo−C(34) and −C(35) distances of 1.946(4) and 1.949(5) Å. These changes in the Mo−C and C−O distances are consistent with the normal synergistic bonding model for transition metal−carbonyl interactions. Each carbonyl maintains almost linear geometry at carbon although the geometry at the beryllium-bound oxygen is bent and features a Be−O(3)−C(33) angle of 147.1(3)°. The synthesis and structure of **8** represent a significant addition to the growing class of isocarbonyl−metal complexes,[27] since it has fairly strong interactions between oxygen and the metal. Its structure is, perhaps, most closely related to the magnesium complex *trans*-Mg(py)$_4$\{(OC)$_3$Mo($\eta^5$-$C_5H_5$)\}$_2$.[28] Analysis of the IR spectrum of this complex in the carbonyl region showed that isocarbonyl−metal complex formation is associated with a decrease in the CO stretching frequency of the lowest carbonyl band, which appears at 1635 cm$^{-1}$ in the case of **8**. A comparison of this frequency with the 1749 cm$^{-1}$ band of NaMo($\eta^5$-$C_5H_5$)(CO)$_3$ shows that the decrease is 114 cm$^{-1}$, which is significantly larger than the 60−90 cm$^{-1}$ range for the magnesium isocarbonyl species.

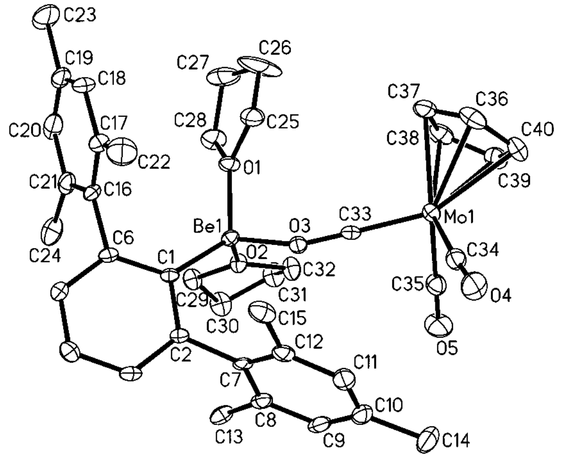

**Figure 8.** Thermal ellipsoid (30%) drawing of **8**. H atoms except those of NH’s are not shown.

The amidinate complexes **9** and **10** (Figures 9 and 10) were isolated from a single reaction mixture. They form part of a large class of amidinate complexes that have attracted consider-

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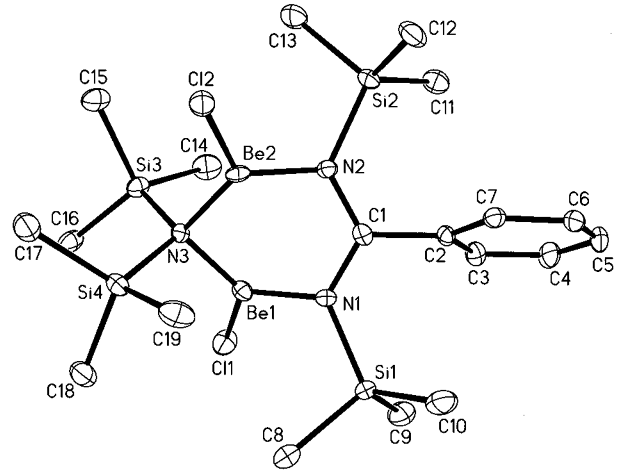

**Figure 9.** Thermal ellipsoid (30%) drawing of **9**. H atoms are not shown.

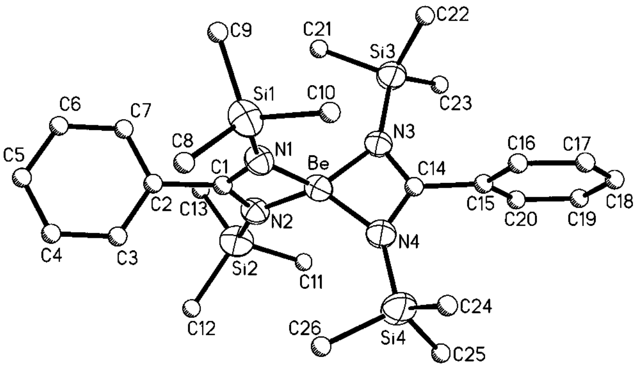

**Figure 10.** Thermal ellipsoid (30%) drawing of **10**. H atoms are not shown.

able recent interest.[29] The bis(amidinate) species **10** is the simpler of the two compounds. The beryllium is coordinated in a distorted tetrahedral fashion to four nitrogens from two bidentate amidinate ligands with Be−N distances in the range 1.723(6)−1.730(6) Å. The N−Be−N angles formed by each ligand are 79.6(3) and 79.7(3)°. The Be−N distances are similar to those in **5**, wherein the nitrogens are four-coordinate and beryllium is three-coordinate. The closest beryllium species available for comparison is the complex Be{N($C_6H_4$-4-Me)C(Ph)C(Ph)N$C_6H_4$-4-Me}$_2$,[30] which also has very similar Be−N bond lengths in the range 1.68(2)−1.73(2) Å. The complex PhC($NSiMe_3$)$_2$(BeCl)$_2$N($SiMe_3$)$_2$, **10**, may be regarded as an association of the uncharacterized entitites ClBeN($SiMe_3$)$_2$ and ClBe($NSiMe_3$)$_2$CPh, which are linked through Be−N bridging to form a six-membered ring composed of three nitrogens, two berylliums, and one carbon atom. The sequence of the internal torsion angles (+20.4°, −46.7°, +20.2°, +23.4°, −48.4°, +20.7°) is in good agreement with a *twist* conformation. The beryllium atoms are both three-coordinate, each being bound to a chlorine and two ring nitrogens. The Be−N distances fall in the range 1.649(6)−1.686(5) Å and are shorter than those in **10** or in the dimer **5** but longer than the 1.577(4) Å in **6**. These variations can be traced, in the main, to differences in the coordination numbers of beryllium and nitrogen. The Be−Cl distances 1.914(5) and 1.926(4) Å are practically identical to those observed in **2a** and **2b**, which also involve three-coordinate beryllium.

**Table 3.** $^9$Be NMR $C_6D_6$ Solution Spectral Data

| | Be coordn no. | δ ppm (*T*/°C) | $w_{1/2}$/Hz |
|---|---|---|---|
| $BeBr_2(OEt_2)_2$ (**1**) | 4 | 3.0 (20) | 47 |
| | | 3.0 (70) | |
| ArBeCl($OEt_2$) (**2**) | 3 | 12.8 (20) | 315 |
| | | 12.5 (70) | 150 |
| ArBeBr($OEt_2$) (**3**) | 3 | 13.4 (20) | 245 |
| | | 13.0 (70) | 145 |
| ArBeSMes*($OEt_2$) (**4**) | 3 | 17.4 (20) | 540 |
| | | 17.1 (70) | 260 |
| ArBeNHSiPh$_3$($OEt_2$) (**6**) | 3 | 12.6 (70) | 285 |
| ArBeN($SiMe_3$)$_2$ (**7**) | 2 | 15.6 (20) | 580 |
| | | 15.7 (70) | 230 |
| PhC($NSiMe_3$)$_2$(BeCl)$_2$N($SiMe_3$)$_2$ (**9**) | 3 | 11.4 (70) | 105 |
| Be{($NSiMe_3$)$_2$CPh}$_2$ (**10**) | 4 | 5.5 (20) | 6.7 |
| Ar(THF)$_2$Be(OC)$_3$Mo($\eta^5$-$C_5H_5$) (**8**) | 4 | 2.7 (70) | 150 |
| $BeCl_2(OEt_2)_2$ | 4 | 2.6 (20) | |
| | | 2.6 (70) | |

**$^9$Be NMR Spectroscopy.** The currently known range of $^9$Be chemical shifts is from δ *ca.* −25 to δ +25.[31,32] Generally speaking, increasing the coordination number of the beryllium results in chemical shift at higher field whereas increasing the electronegativity of a beryllium substituent results in a shift to lower field. $^9$Be NMR data for **1**−**4** and **6**−**10** are presented in Table 3. The shifts of the four-coordinate species **1**, **8**, and **10** are in the narrow range 2.7−5.5 ppm and are consistent with those previously observed for other four-coordinate beryllium complexes.[19,31−34] It is notable, however, that the shift observed for **1** is at lower field than that for $BeCl_2(OEt_2)_2$ even though chlorine is more electronegative than bromine. In addition, the shift of the bromine derivative **3** is lower than that of the corresponding chlorine species **2** so that effect seems to be a consistent one. Lowering the coordination number of the beryllium complex from 4 to 3 results in a shift to lower field. Thus, the complexes **2**−**4**, **6**, and **9** appear *ca.* 10 ppm further downfield than **1**, **8**, and **10**. The shifts observed for the three-coordinate species **2**, **3**, **6**, and **9** are in the relatively narrow range δ 11.4−13.4 while the thiolate **4** appears at δ 17.4, which seems anomalous in view of the lower electronegativity of sulfur in comparison to that of the halides or nitrogen. The two-coordinate complex **7** is observed at 15.6 ppm, which currently appears to be the only $^9$Be NMR chemical shift available for a two-coordinate species. Its chemical shift is close to that observed for the thiolate complex **4**, suggesting that the latter might also be dissociated in solution. The shift of **7** is, however, lower than those of the other three-coordinate complexes **2**, **3**, **6**, and **9**. A notable feature of the data in Table 3 is that the width of the peaks for the two- and three-coordinate species are up to 2 orders of magnitude greater than those for the four-coordinate complexes. The narrowest peak is observed for the four-coordinate complex **10**, which is closest to idealized tetrahedral geometry, where quadrupolar coupling is expected to be near zero.

**Acknowledgment.** We are grateful to the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support.

**Supporting Information Available:** Tables giving full crystallographic data and data collection parameters, atom coordinates, bond distances, bond angles, anisotropic thermal parameters, and hydrogen coordinates for **1**−**10** (104 pages). Ordering information is given on any current masthead page.

IC970319T

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